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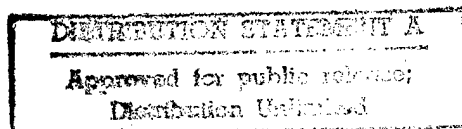
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Applications of Cd_2SnO_4 Transparent Conducting Oxides in CdS/CdTe Thin-Film Devices

X. Wu, P. Sheldon, T.J. Coutts, D.H. Rose,
and H.R. Moutinho

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APPLICATION OF Cd_2SnO_4 TRANSPARENT CONDUCTING OXIDES IN CdS/CdTe THIN-FILM DEVICES

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ABSTRACT

An unusual processing scheme has been developed for preparing single-phase cadmium stannate (Cd_2SnO_4 or CTO) films. Cd_2SnO_4 transparent conducting oxide (TCO) films have several significant advantages over conventional TCOs when applied to CdS/CdTe thin-film devices. They are more conductive, more transparent, have lower surface roughness, are patternable, and are exceptionally stable. Cd_2SnO_4 -based CdS/CdTe polycrystalline thin-film solar cells with efficiencies of 14% have been fabricated. Preliminary cell results have demonstrated that device performance can be enhanced by replacing the SnO_2 layer with a Cd_2SnO_4 TCO film.

INTRODUCTION

Cadmium telluride has long been recognized as a promising photovoltaic material for thin-film solar cells because of its near optimum bandgap of 1.5 eV and its high direct absorption coefficient. Small-area CdS/CdTe heterojunction solar cells with efficiencies of more than 15% and commercial-scale modules with efficiencies of 9% have been demonstrated [1,2]. In the past, little attention has been paid to the transparent conducting oxide (TCO) layer of this device structure. Conventional TCOs, primarily SnO_2 films, typically have been used as the front collector in CdS/CdTe cells and modules. However, SnO_2 films, deposited using the commercially viable SnCl_4 chemistry, have a resistivity of $\sim 5\text{--}8 \times 10^{-4} \Omega\text{-cm}$. This yields films with an average transmission of 80% and a sheet resistivity of about $10 \Omega/\text{square}$. Although this may be satisfactory for small-area devices and first-generation modules, it does not provide adequate design latitude when trying to optimize either device performance or manufacturing costs. For example, reducing the TCO resistivity by a factor of two could allow for a TCO film that retains the same sheet resistance as the inferior TCO, yet is half as thick. This would improve the transmission and ultimately improve device performance by increasing the short-circuit current density (J_{sc}). Alternatively, a film with transmission properties similar to those of the inferior TCO, but half the sheet resistance, could be used. This would have the advantage of reducing the number of interconnects required, thereby improving throughput, reducing interconnect losses, and reducing manufacturing costs. For these reasons, it is desirable to improve the

performance of the TCO films for CdS/CdTe solar cell applications.

Nozik and later Haacke et al. were the first to report Cd_2SnO_4 TCO films deposited by r.f. sputtering [3,4]. Recent improvements in r.f. sputter-deposited Cd_2SnO_4 and post-deposition processing have yielded films with superior properties [5,6]. In this work, we describe cadmium stannate films that we have optimized for CdS/CdTe devices. Cadmium stannate films have several significant advantages over conventional TCOs. They are more conductive, more transparent, have lower surface roughness, are patternable, and are very stable. Cd_2SnO_4 -based CdS/CdTe polycrystalline thin-film solar cells with efficiencies of 14.0% have been fabricated. Preliminary cell results have demonstrated that device performance can be enhanced by replacing the SnO_2 layer with a Cd_2SnO_4 TCO film.

EXPERIMENTAL

Single-phase Cd_2SnO_4 films have been prepared using an unusual processing scheme developed in our laboratory [5,6]. CTO films were prepared by r.f. magnetron sputtering from a commercial hot-pressed-oxide target with a composition of 33 mol% SnO_2 and 67 mol% CdO . Corning 7059 glass or soda-lime glass substrates were placed on a water-cooled sample holder parallel to the target surface. Deposition was performed at an oxygen partial pressure of $10\text{--}20 \times 10^{-3}$ torr at nominally room temperature, and a deposition rate of $\sim 100 \text{ \AA}/\text{min}$. After deposition, all samples were annealed in a tube furnace in an Ar or Ar/ CdS atmosphere at elevated temperatures of $580\text{--}680^\circ\text{C}$ for 10–30 minutes. The electrical, optical, and compositional properties of CTO films were characterized using Hall effect, optical and infrared spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM) measurements. We have also processed a limited number of CTO-based CdS/CdTe devices. In these devices, the CTO film thickness varied from 2500 \AA to 6000 \AA , with resistivities of 7 to $3 \Omega/\text{sq.}$, respectively. The CdS thickness was $800\text{--}1000 \text{ \AA}$, and the CdTe film thickness was around $10 \mu\text{m}$. The details of the CdTe cell fabrication procedure is described elsewhere [7].

RESULTS AND DISCUSSION

Cadmium stannate material properties

The conductivity of TCOs can be improved by either increasing the carrier concentration or the electron mobility. By optimizing sputtering and post-annealing conditions of CTO films, electron mobilities as high as $65 \text{ cm}^2/\text{Vs}$ have been achieved for a carrier concentration of $2 \times 10^{20} \text{ cm}^{-3}$. Even at a carrier concentration of $\sim 9 \times 10^{20} \text{ cm}^{-3}$, mobilities as high as $55 \text{ cm}^2/\text{Vs}$ have been observed. These mobilities are 2-3 times higher than those of commercial SnO_2 films doped to similar levels. Free carriers are thought to result from oxygen deficiencies in the films, accommodated either as oxygen vacancies or cadmium interstitials, or a combination of both. This results in resistivities as low as $1.3 \times 10^{-4} \Omega\text{-cm}$ in the best CTO samples [7]. This is almost seven times lower than conventional SnCl_4 -based SnO_2 films and 2.5 times lower than the best SnO_2 films deposited using tetramethyltin-based precursors ($\rho_{\text{TMT}} = 3.3 \times 10^{-4} \Omega\text{-cm}$). Table 1 shows a comparison of electrical properties of more typical Cd_2SnO_4 films prepared at NREL and commercially available SnCl_4 -based SnO_2 films. The reduced resistivity of CTO films provides a clear advantage. For example, a sheet resistance of $\sim 9 \Omega/\text{sq.}$ can be achieved with a CTO film of less than 2000 \AA , as compared to nearly $10,000 \text{ \AA}$ for the SnO_2 film. Alternatively, thicker films can be used to reduce the device series resistance, thus improving its fill-factor and efficiency. Reducing the series resistance in modules is of particular interest, because manufacturers can optimize cell width between laser scribe lines, thereby reducing I^2R and optical losses.

Table 1. Electrical Properties of CTO and SnO_2 Films.

Sample	t (\AA)	ρ ($\Omega\text{-cm}$)	R _s ($\Omega/\text{sq.}$)
SnO_2 (SnCl_4)	10000	8.6×10^{-4}	8.6
CTO245	1900	1.8×10^{-4}	9.5
CTO229	2550	1.8×10^{-4}	6.9
CTO250	3950	2.0×10^{-4}	5.0
CTO252	6500	2.2×10^{-4}	3.1

Cd_2SnO_4 films have significantly better optical properties than conventional SnO_2 films. This is, in part, due to the lower resistivities, which allow thinner films to be used. For example, Fig. 1 shows the transmittance and absorbance of Cd_2SnO_4 and SnO_2 films with similar sheet resistivities ($\sim 10 \Omega/\text{sq.}$). The CTO film has superior transmission when compared to the SnO_2 film, even though the CTO film has a slightly lower sheet resistivity. The absorbance of the CTO film, in the visible range, is much smaller than that of the SnO_2 film. For example, at 600 nm , the absorbance of the CTO film is only 0.8% , compared to

12.2% for the SnO_2 film. This appears to be due to the unusually high electron mobility of CTO films. The improved transmission and absorbance of CTO films is ideal for the superstrate structure of CdS/CdTe devices and will ultimately yield improved short-circuit currents.

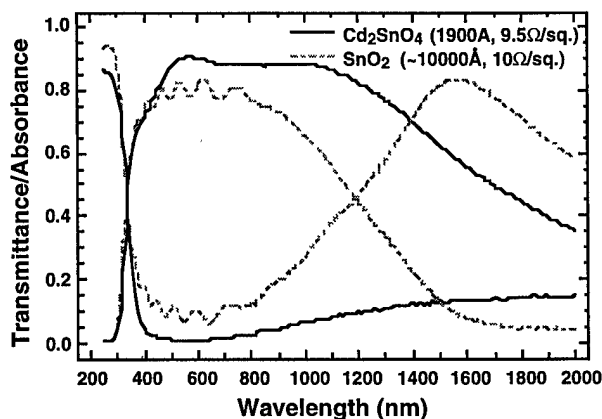


Fig. 1. Transmission and absorbance of a CTO and SnO_2 film with a sheet resistivity of $\sim 10 \Omega/\text{square}$.

Fig. 2 shows the absorbance data of the four CTO films listed in Table 1. As expected, the absorbance increases with an increase in CTO film thickness. However, more interesting is the shift in optical bandgap to longer wavelengths with increasing CTO film thickness. The thinnest CTO film has a bandgap that is near that of a SnO_2 film (see Fig. 1). We do not believe that the bandgap shift is a result of the Moss-Burstein shift, because the thinnest CTO film has the lowest carrier concentration (the plasma edge is also located at longer wavelengths). Although we do not completely understand this effect, we believe that it may be a result of changes in film composition throughout its thickness. X-ray photoelectron spectroscopy (XPS) and XRD analysis is under way to test this hypothesis.

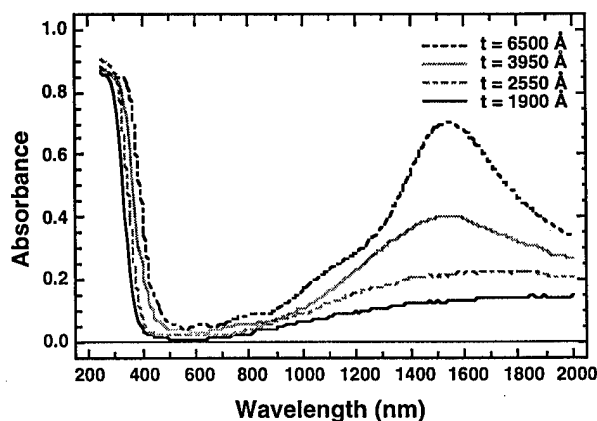


Fig. 2. The absorbance of four CTO samples with different thickness.

TCO surface roughness is also an important parameter when considering device processing issues. It is well known that in heterojunction solar cells, higher short-circuit currents can be obtained by reducing the window layer absorption. In CdS/CdTe cells, this is achieved by reducing the CdS thickness to yield an enhanced blue spectral response. Unfortunately, as the CdS is thinned, pinholes form and cause localized CdTe/SnO₂ junctions with inferior open-circuit voltages and fill factors. The probability of forming pinholes likely increases as the TCO surface roughness increases. AFM measurements indicate an average surface roughness of ~210Å for SnCl₄-based SnO₂ films. In contrast, the Cd₂SnO₄ films have a very smooth surface with an average roughness of ~20Å, an order of magnitude lower than that of the SnO₂ film [7]. This reduction in surface roughness could lead to improved device performance.

Cadmium stannate films also have excellent adhesion and thermal stability [7]. Our experimental results show that the resistivity of a SnCl₄-based SnO₂ film degrades when annealed in an Ar ambient for 20 minutes at a temperature of 500°C. In contrast, CTO films are stable up to temperatures as high as 650°C [7]. This is particularly important when considering that close-spaced sublimation (CSS) CdTe deposition temperatures can exceed 600°C.

The properties of CTO films described above are well correlated to the microstructure of the film. For example, Fig. 3 shows typical XRD data for an as-deposited and an Ar/CdS-annealed CTO film. The as-deposited films are amorphous, exhibit extremely high resistivities (~5000 Ω-cm), have a lower optical bandgap, and have poor transmission characteristics. After the Ar/CdS anneal, the film crystallizes into a single-phase spinel structure with optical and electrical properties similar to those described in Table 1. After crystallization, there is no evidence that secondary phases, such as CdO, SnO₂,

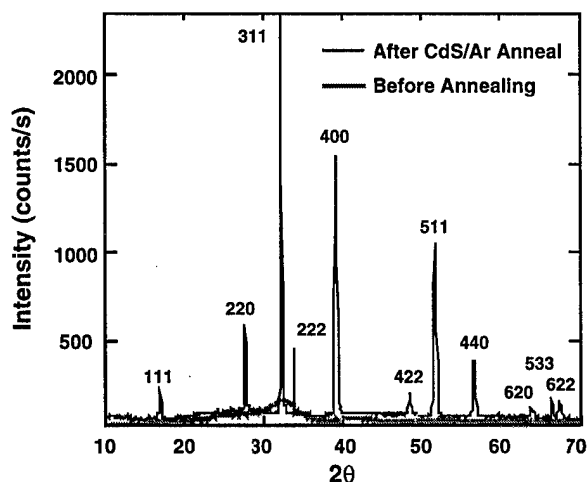


Fig. 3. Typical XRD pattern of an as-deposited and an annealed Cd₂SnO₄ film.

or CdSnO₃, form in our CTO films. We find that Ar/CdS anneals drastically reduce the temperature required for film recrystallization. We have demonstrated the same improvement in CTO film properties at 580°C anneals on low-cost, soda-lime glass, achieving a resistivities as low as 1.84×10^{-4} Ω-cm. This value is similar to values obtained for the higher-temperature process.

Cadmium-stannate-based CdS/CdTe devices

The improved material properties of CTO films provide a strong impetus to incorporate them in a superstrate device structure. We find that processing parameters that were optimum for SnO₂-coated glass are not suitable for CTO-coated glass. This is particularly evident when comparing the post-CdTe-deposition CdCl₂ anneal. CdTe/CdS/SnO₂ devices that have not been CdCl₂ treated, exhibit open-circuit voltages (V_{oc}) of about 550 mV. To obtain open-circuit voltages of >800 mV, it is necessary to soak the sample in a saturated CdCl₂:MeOH solution with a concentration of greater than 50% (typically between 50%-100%) and subsequently anneal the film at 400°C. At higher concentrations (near 100%), the films exhibit severe adhesion problems, thereby reducing yields. In contrast, CdTe/CdS/Cd₂SnO₄ devices require a lower CdCl₂ concentration. CdTe/CdS/Cd₂SnO₄ devices, which have not been CdCl₂-treated, exhibit open-circuit voltages as high as 650 mV (nearly 100 mV higher than the SnO₂-based devices). Furthermore, CdCl₂ concentrations as low as 25% are adequate to provide a V_{oc} of >800 mV.

To compare the differences between Cd₂SnO₄- and SnO₂-based CdTe cells, a set of CdTe cells was prepared using identical cell fabrication procedures. The cells were soaked in a saturated 25% CdCl₂:MeOH solution for zero to 20 minutes and then annealed at 400°C for 30 minutes. As shown in Fig. 4, the efficiency of Cd₂SnO₄-based devices is always higher than that of SnO₂-based devices

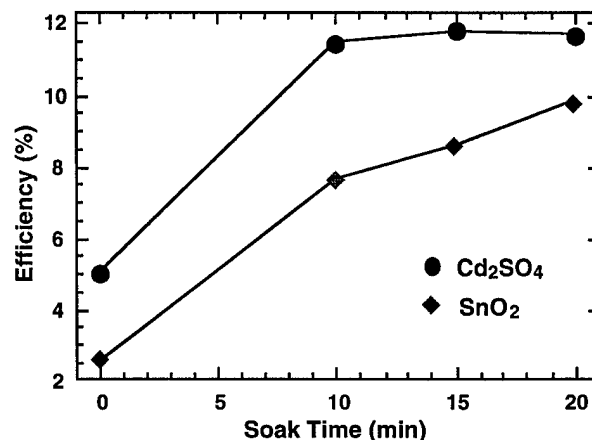


Fig. 4. CdTe cell efficiency as a function of soak time for a 25% CdCl₂:MeOH solution (note: under different processing conditions, higher efficiency devices have been achieved both with and without a CdCl₂ treatment).

for a given soak time. Earlier work has shown that this is also true when varying the CdCl_2 concentration and keeping the soak time constant [7]. This result could, in part, be caused by the reduced surface roughness of the CTO film. However, it is likely that the chemistry of the CTO/CdS interface is also an important factor. Fig. 4 also indicates that the efficiency of CTO-based CdS/CdTe devices is less dependent on the CdCl_2 heat-treatment. This result suggests the potential for improved process reproducibility and yield.

In addition to improved device performance at lower CdCl_2 concentration treatments, CTO-based devices have better adhesion than their SnO_2 counterparts. Although the SnO_2 -based devices improve with increased CdCl_2 concentrations, the adhesion degrades. At 100% CdCl_2 concentrations, most CdTe films will blister and eventually separate from the SnO_2 superstrate. Although CTO-based devices require lower CdCl_2 concentrations for optimum performance, most devices remain intact after a 100% CdCl_2 treatment. For example, in a set of 16 CTO-based devices treated at 100% CdCl_2 , only 2 out of 16 devices resulted in adhesion failure. This could have significant process yield ramifications.

As described earlier, the improved transmission and absorbance of CTO films is ideal for superstrate CdS/CdTe devices and should yield improved device J_{sc} . Fig. 5 shows the relationship between the TCO film transmission and the resulting J_{sc} , for devices deposited on both CTO and SnO_2 superstrates. It is clear that by replacing the SnO_2 film with a CTO superstrate, the reduced optical losses yield an increase in J_{sc} . For example, replacing the 10,000Å SnO_2 film with a 2500Å CTO film yielded an increase in J_{sc} of more than 1.5 mA/cm². It is important to note that devices fabricated on the thicker CTO films always gave the highest fill factors. Fill factors of 75% have been achieved using 6000Å-thick CTO films in ~1 cm² devices. These films have resulted in devices with

efficiencies of up to 14% (V_{oc} =0.805 V, J_{sc} =23.5 mA/cm², FF=74%), as measured under standard conditions. Therefore, thicker CTO films, with lower sheet resistivities, may be better suited for module applications.

CONCLUSIONS AND FUTURE WORK

Cd_2SnO_4 transparent conducting oxides have several significant advantages over conventional tin oxides. They are more conductive, more transparent, have a lower surface roughness, are patternable, and are exceptionally stable. Cd_2SnO_4 -based CdS/CdTe polycrystalline thin-film solar cells with efficiencies of 14.0% have been prepared for the first time. The preliminary cell results have demonstrated that, by replacing the conventional SnO_2 with a Cd_2SnO_4 film, CdS/CdTe device performance can be enhanced. Cd_2SnO_4 -based CdTe cells yield higher short-circuit currents and efficiencies, and are less dependent on the CdCl_2 treatment than their SnO_2 counterparts. We believe that the performance of Cd_2SnO_4 -based CdS/CdTe cells is far from optimized. Future work will concentrate on improving the efficiency of Cd_2SnO_4 -based CdS/CdTe cells through the optimization of Cd_2SnO_4 film preparation and cell fabrication and on developing more manufacturable processes.

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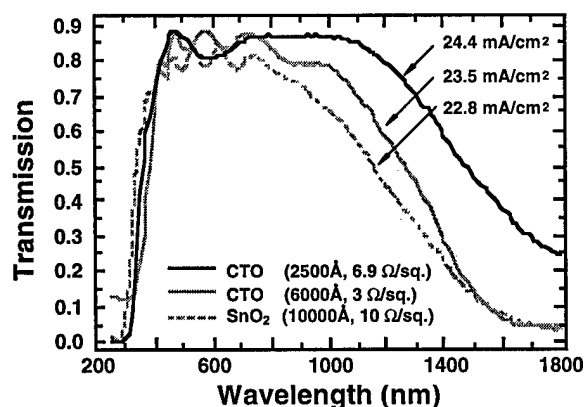


Fig. 5. Relationship between J_{sc} and transmission of SnO_2 and CTO films.